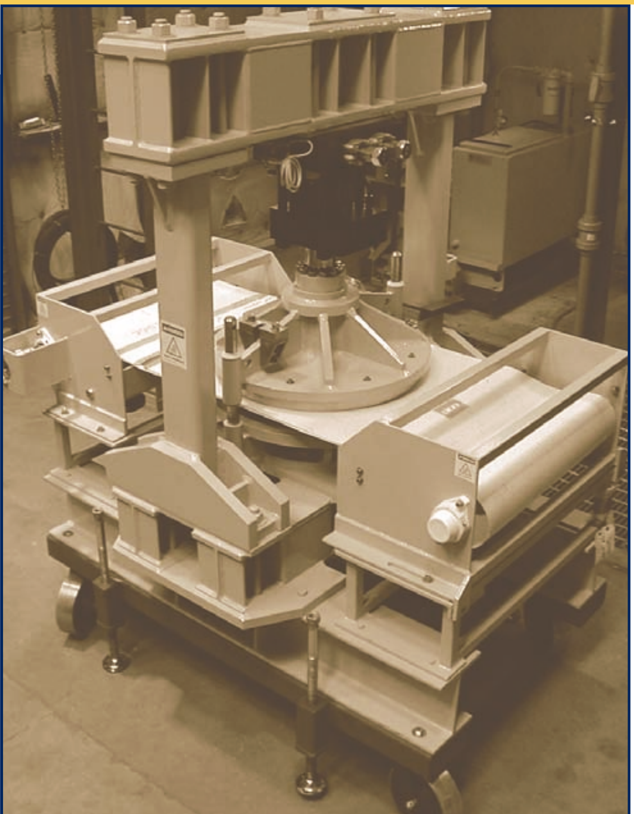
Washing Away Bioprocessing Cost

For Sustainable Transportation Biofuels

Pressurized Hot Wash Improves Cellulosic Ethanol Technology



Nick Nagle, NREL/PIX 11550

The Biofuels Program Pressurized Hot Wash Process uses this pressurized equipment from Pneumapress Filter Corporation to allow separation and washing with above boiling—up to 160°C—but still liquid, water. This prevents reprecipitation of material solubilized during pretreatment, leaving solids that enzymatically hydrolyze and ferment more readily.

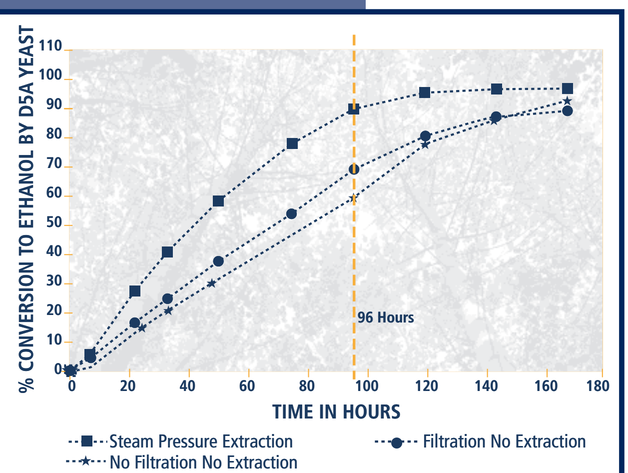
Thermochemical pretreatment is a key step in the process for converting lignocellulosic biomass to fuel ethanol and other valuable chemicals. U.S. Department of Energy Biofuels Program researchers have found that adding a Pressurized Hot Wash (PHW) step immediately following pretreatment—while the pretreated material is still at high temperature and pressure—significantly improves the overall process. The "hot-washed" pretreated material can be more efficiently digested by cellulase enzymes. Additionally, soluble lignins with potentially valuable unique reactive properties are separated out.

Background Current commercial ethanol production starts with starch or sugar. These carbohydrates are easy to ferment, but are only a very small portion of available plant material and have value for food production. The vast majority of biomass material is lignocellulosic—a mixture of cellulose, hemicellulose, and lignin. While more challenging to convert than starch, cellulose and hemicellulose are long chains (polymers) of sugar molecules that can be fermented or otherwise processed biologically once they are broken down (hydrolyzed) into their component sugars. Pretreatment is the first major step in meeting this challenge.

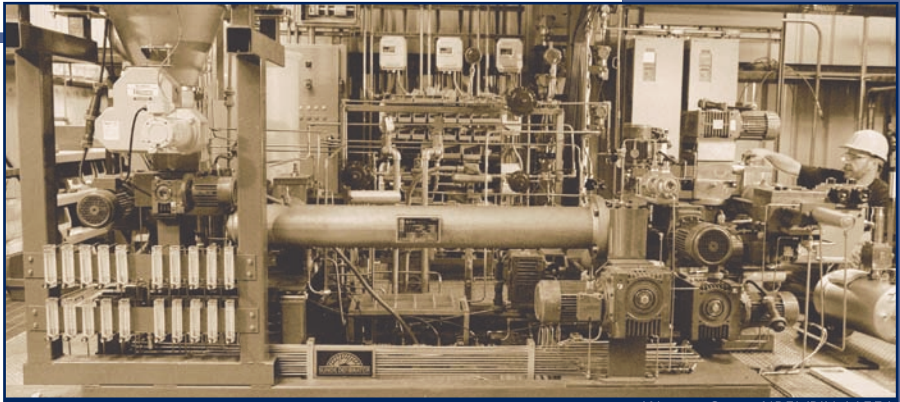
Cell walls of lignocellulosic biomass are essentially structured with a sheath of lignin and hemicellulose surrounding a core of cellulose. This makes it more difficult chemically and biologically to get at the cellulose. Pretreatment solubilizes the hemicellulose or the lignin or both. This enhances the digestibility of the remaining solid cellulose by enzymatic hydrolysis. Some of the pioneer lignocellulosic bioethanol plants will thermochemically hydrolyze the cellulose as well, but Biofuels Program analysis shows that biological enzymatic hydrolysis of cellulose should be more cost effective in the long run. Dilute sulfuric acid pretreatment is highly effective for hydrolyzing the hemicellulose, but leaves most of the lignin with the cellulose solids—or so was previously thought. Other pretreatments are more effective at solubilizing the lignin, but less effective at hydrolyzing the hemicellulose.

How it Works Without Pressurized Hot Wash, the liquid hydrolyzate (mostly xylose and other hemicellulose sugars and dilute acid) and solids (mostly cellulose and lignin) are generally not mechanically separated before enzymatic hydrolysis of the cellulose. The temperature and pressure of the liquid and solids are allowed to return to ambient. Biofuels Program researchers hypothesize that more lignin is solubilized by the dilute-acid process than was previously realized, and that, released from the temperature and pressure of the pretreatment reactor, some of this lignin and possibly some xylan reprecipitates back onto the cellulose, interfering with subsequent cellulose hydrolysis.

With Pressurized Hot Wash, immediately after pretreatment, the pretreated biomass is first pressed to separate liquid hydrolyzate from the solids. Then—while still under pressure, so the temperature can be kept about 130°C—hot water is added to the hydrolyzate/solid mixture. Any solubilized lignin is now washed away from the cellulose, along with the xylose, leaving it more "digestible" for enzymatic hydrolysis. The difference is so dramatic that hardwood feedstocks processed with dilute-acid



Improved digestibility of yellow poplar with Pressurized Hot Wash.



Warren Gretz, NREL/PIX 11551

This pretreatment reactor, built by Metso Corporation, is derived from standard pulping industry equpment. This pretreatment hydrolyzes hemicellulose and solubilizes some lignin. The Pressurized Hot Wash process seperates these materals before they can reprecipitate. This system uses dilute sulfuric acid at increased temperture and pressure, but Pressurized Hot Wash may work well with any pretreatment system.

pretreatment followed by PHW were dubbed “Wonderwood.” They produced higher yields of ethanol and required only 4 days instead of 7 days in a combined enzyme hydrolysis-fermentation process. Alternatively, the amount of cellulase enzyme used—one of the most expensive elements of the process—might possibly be reduced. Based on this enhanced performance, the cost of producing ethanol from lignocellulosic feedstocks should drop significantly with PHW.

Lignin can be sticky stuff, drawing comparison to glue. It also goes through a phase change between a molten state such as you could imagine for glass or plastic (the glue) and a more solid state at ambient temperatures. Biofuels Program researchers believe that while not as hot as the 180°C or so needed to hydrolyze the hemicellulose in the pretreatment reactor, the 130°C heat of the PHW process is enough to stay above the “glass transition” temperature of lignin. This allows the now somewhat soluble lignin to flow away with the hemicellulose sugars and wash water before it has a chance to reprecipitate back onto the pretreated solids. This is what makes the cellulose easier to hydrolyze and makes the subsequent hydrolysis and fermentation so much more effective.

Biofuels Program researchers are currently applying the PHW process to corn stover—a main focus of the program. PHW is also well suited to the “sugar platform biorefinery” concept of producing a suite of different products from lignocellulosic material once it is broken down into component sugars. The five-carbon xylose from hemicellulose is physically as well as chemically separated from the six-carbon glucose from cellulose. This makes it more likely that different end-products could be made from the different sugars. Also, the solubilized portion of lignin in the hydrolyzate can be readily recovered and may be ideal for chemical production. The benefits of the Pressurized Hot Wash process have been demonstrated with dilute-acid pretreatment, but might apply to other pretreatment technologies as well.

The Pressurized Hot Wash process is a semi-batch, sub-reaction-temperature, pressurized-rinse separation. It is the product of a combination of basic theoretical understanding, economic necessity, and practicality. Initial work on the PHW process grew out of work on two-stage, percolation, and continuous-flow pretreatment designs. By identifying and taking advantage of the fact that different portions of the hemicellulose required different levels of severity to hydrolyze, these processes achieved excellent yields. They appeared, however, to be difficult to scale up to industrial levels and their projected economics were disappointing, in large part because of the large volumes of high-temperature steam needed. By switching to batch processing and a not-quite-so-hot, separation and washing step, PHW makes the necessary equipment less complicated, reduces the amount of energy needed to heat steam, and provides a workable technology.

Using Pressurized Hot Wash

Pressurized Hot Wash technology is covered under National Renewable Energy Laboratory Patents 6,022,419 and 6,228,177 relating to counter-current and two-stage pretreatment, but is available for use under license or cooperative agreement. The Biofuels Program welcomes interest in investigating PHW for pretreatment processes other than dilute sulfuric-acid, for feedstocks other than stover, or for products other than ethanol, and for licensing it for commercial production.

References

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